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14. ABSTRACT In this project, we: (1) demonstrated colloidal Quantum Dot (QD) based vertical-cavity surface emitting lasers (VCSELs) with record low thresholds, (2) engineered the local density of optical states (LDOS) in 1D waveguides to control the emission of randomly oriented QDs, (3) demonstrated silica cladding of commercial QDs, and thus broadened the range of QD sources suitable for on-chip integration using electrostatic self-assembly methods, (4) demonstrated a robust, reusable platform of alumina templates for the precise placement of single colloidal QDs, (5) built a custom scanning confocal microscope setup capable of performing large-scale characterization of the lifetime and g2 autocorrelation of individual QD emission in self-assembled arrays, and (6) integrated colloidal QDs in dielectric waveguides and near resonant nanostructures.					
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OBJECTIVE: The objective of this research program was to develop a cavity-free architecture for waveguide-integrated single photon sources and optical signal processing at the few to single photon level.

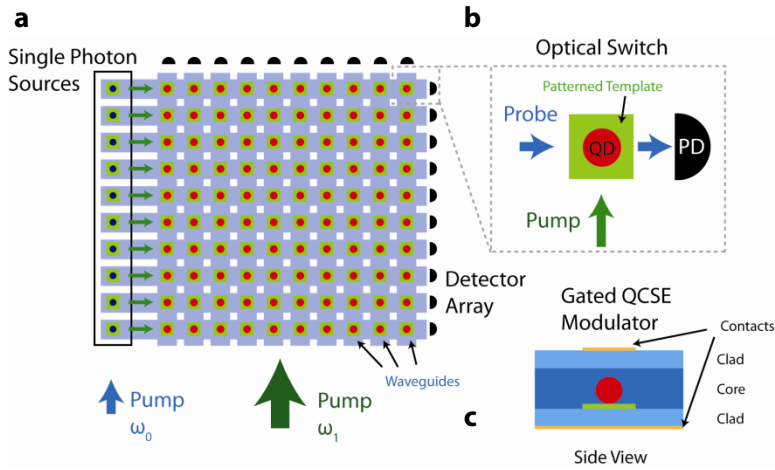


Figure 1: Schematic Design of Matrix-Addressable Quantum Dot Architecture

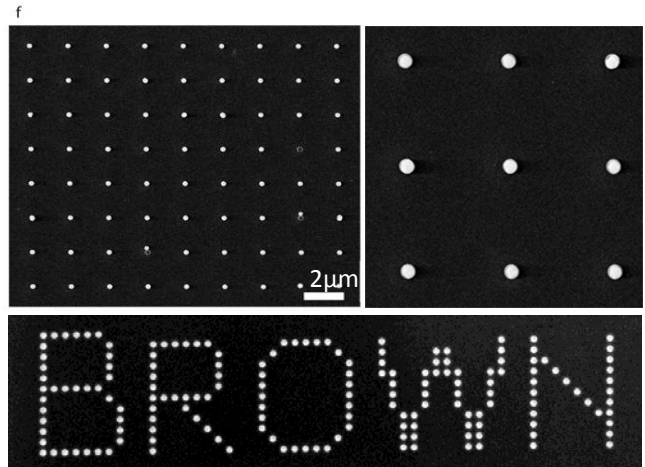
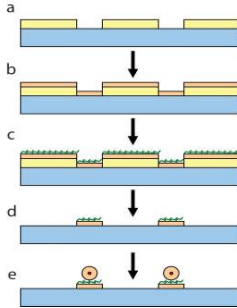
(a) an extended line of small diameter QDs are pumped by a pulsed diode to produce single photons which are then directed via waveguides to a matrix addressable QD switch array; (b) a three terminal optical switch wherein a pump beam is used to modulate the transmission of a weak probe; (c) possible design for a spectral modulator based on the quantum-confined Stark effect.

APPROACH: Our scalable approach built on the Nurmikko lab's recent development of highly-ordered II-VI quantum dot arrays through combined dielectric encapsulation and electrostatic self-assembly [Q. Zhang, C. Dang, H. Urabe, J. Wang, S. Sun, and A. Nurmikko, "Large ordered arrays of single photon sources based on II-VI semiconductor colloidal quantum dot." *Opt. Express* **16**, 19592 (2008)]. This work already demonstrated that such dot arrays can serve as scalable room-temperature single photon sources. By integrating these dielectric-clad quantum dots into an addressable waveguide matrix, this research program aimed to help dramatically reduce the infrastructure required for low-photon number optical switching.

Figure 2. Electrostatic self-assembly of silica-clad quantum dots with single-particle resolution.

a-e) Process Flow Diagram.

We begin (a) with a layer of patterned PMMA resist produced by electron-beam lithography. Then we (b) deposit a thin SiO₂ film (20nm thick) by ion-beam sputtering and (c) use dip-coating techniques to assemble a monolayer of polyelectrolyte (PDDA) molecules on the SiO₂ surface. (d) Lift-off of the PMMA film in acetone leads to PDDA covered SiO₂ pad. Finally, (e) immersion into silica-clad QD ethanol solution results in spatially selective settlement of a single QD on each pad.



f) Scanning Electron Micrographs of resulting Highly Ordered Array. Each bright spot denotes an individual silica-clad quantum dot; the diameter of each silica-clad is approximately 220nm. Note that only a small fraction (<4%) of the particles are accidentally displaced from the target site, exposing the PDDA-covered SiO₂ pad. Zoomed image demonstrates the placement accuracy, and text illustrates the versatility for more complex patterns. [Adapted from C. Dang *et al.* *Opt. Express* **16**, 19592 (2008)]

Summary of Program Accomplishments: During this research program, we focused on two main areas of research: (1) Materials Synthesis and Fabrication for Engineering QD Emission, and (2) Statistical Studies using the QD Array Architecture for Nanophotonic Integration. Our six major technical accomplishments within these areas can be categorized as follows:

(1) Materials Synthesis and Fabrication Techniques for Engineering QD Emission

- Demonstrated the first colloidal-QD-based vertical-cavity surface emitting lasers (VCSELs) with record low thresholds.
- Engineered the local density of optical states (LDOS) in 1D waveguides to control the emission of randomly oriented QDs.
- Demonstrated silica cladding of commercial QDs, and thus broadened the range of QD sources suitable for on-chip integration using the electrostatic self-assembly method.

(2) Statistical Studies Using QD Array Architecture for Nanophotonic Integration

- Demonstrated reliable and reusable self-assembly of silica-clad QDs on high isoelectric point Al_2O_3 templates.
- Built a custom scanning confocal microscope setup capable of performing large-scale characterization of the lifetime and $g^{(2)}$ autocorrelation of individual QD emission in self-assembled arrays.
- Integrated colloidal QDs in dielectric waveguides and near resonant nanostructures.

On the subsequent pages, we provide a detailed summary of these six main technical outcomes.

Focus 1

Demonstration of Colloidal QD-VCSEL

We leveraged colloidal QDs to enable new device applications for these scalable materials. Specifically, we demonstrated the first colloidal QD based vertical-cavity surface-emitting lasers (VCSELs). Using high quality colloidal QDs, we were able to engineer densely packed QD films that exhibit single-exciton gain and low threshold lasing, as shown in Figure 3. These results coupled with the tunable QD gain spectra enabled the direct realization of red, green, and blue colloidal QD lasers. This work was published in *Nature Nanotechnology* [C. Dang, J. Lee, C. Breen, J. S. Steckel, S. Coe-Sullivan, and A. Nurmikko. "Red, green and blue lasing by single-exciton gain in colloidal quantum dot films." *Nature Nano.* **7**, 335 (2012)] and highlighted by an SPIE Newsroom brief invited review [C. Dang and A.V. Nurmikko, "Single-exciton gain enables red, green, and blue colloidal quantum dot lasers." *SPIE Newsroom* DOI: 10.1117/2.1201208.004441 (2012)].

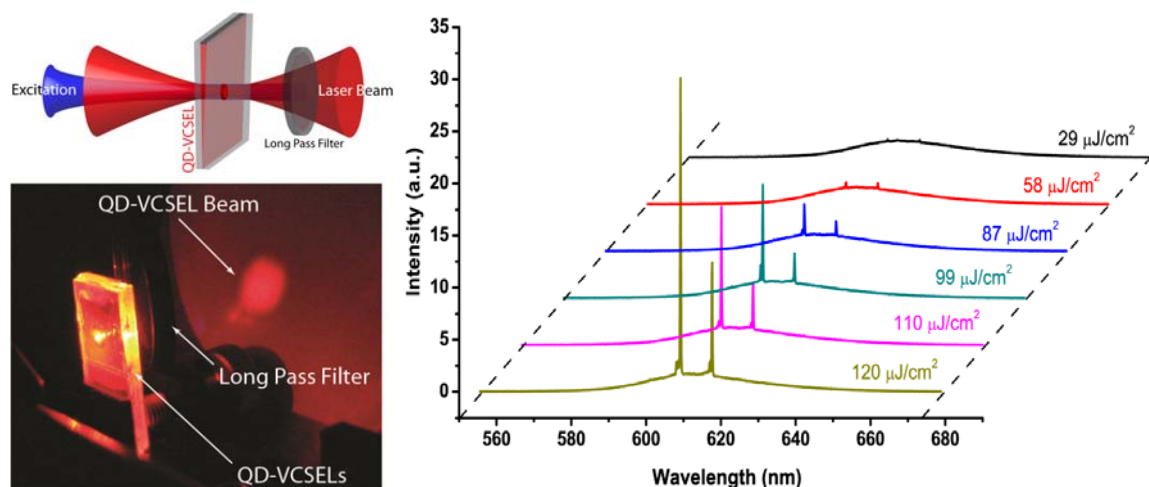


Figure 3: Demonstration of first colloidal quantum dot VCSEL. From C. Dang et al. *Nature Nanotech.* **7**, 335 (2012)

LDOS Engineering of QD Emission

We demonstrated a simple technique to effectively "orient" the emission from randomly-oriented QDs within dielectric thin-films. By engineering the local density of optical states (LDOS) within 1D waveguides, we were able to control the dominant direction and polarization of the emitted light. After optimizing deposition conditions for safely embedding colloidal QDs in high index dielectric thin films, we performed parametric studies of QD emission within varying thickness planar waveguides. In good agreement with our theoretical LDOS based calculations, these experiments confirmed the preferential emission of randomly-oriented QDs into specific modes, as shown in Figure 4. These results also highlighted the importance of waveguide thickness for directing QD emission into desired modes and validated the use of our LDOS calculations for the design of two-dimensional ridge waveguides for the matrix-addressable QD arrays.

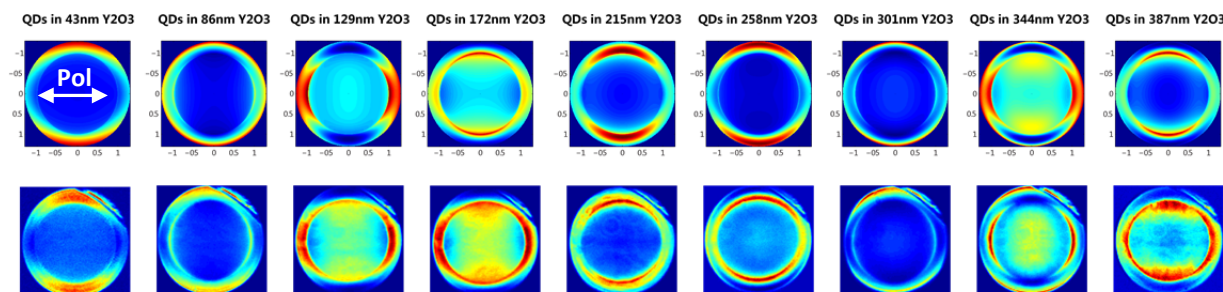


Figure 4: Engineering the LDOS to control QD emission (top row: Theory, bottom row: Experiments).

By varying the thickness of 1D waveguide structures, we can preferentially couple light emission from randomly oriented QDs into specific emission modes.

Demonstration of Silica-Cladding with Commercial QDs

We expanded our scalable wet chemistry techniques for encapsulating single QDs within silica shells, the first step for our electrostatic self-assembly method. In particular, we demonstrated silica-encapsulation of commercially-available QDs from Invitrogen and NN-Labs, as shown in the Figure 5. These QDs are available in large quantities, exhibit high quantum yield, and can be stabilized in aqueous solutions. Some commercial QDs also have a polymer coating that can provide protection from solvents during and after silica shell growth. Note that expanding the silica cladding method to commercial QDs opens the potential for more scalable fabrication, broadens the range of available QDs, and significantly enhances the likely impact of this work.

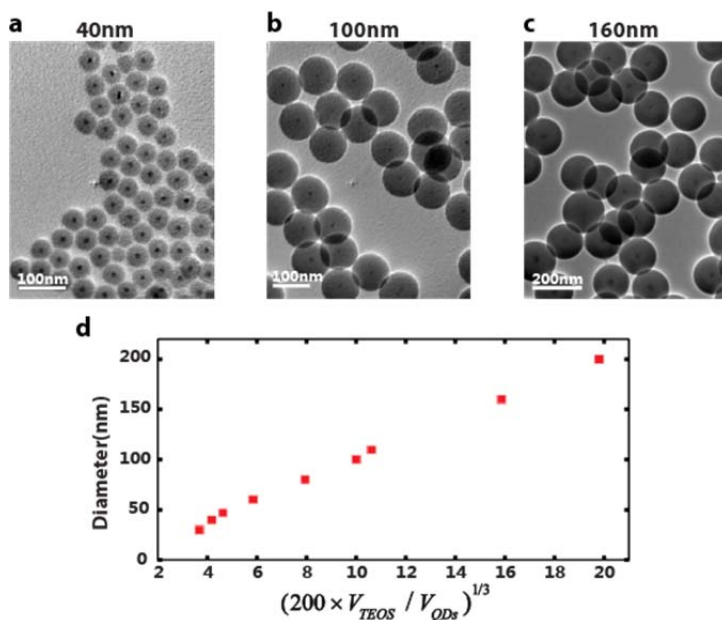


Figure 5: Silica-encapsulation of commercially available polymer-coated QDs.

(a)-(c) TEM showing individual NN-Labs CZ600 QDs each coated with a different radius silica cladding. (d) Silica shell thickness as a function of the cube root ratio of Tetraethyl Orthosilicate (TEOS) to QDs. TEOS is the precursor providing SiO_2 in the silica growth.

Focus 2

Fully Optimized, Robust, Reusable Inorganic Template

Although the original polymer-based templates enabled high-efficiency self-assembly, the PDDA polymer surface was susceptible to contamination and degradation during liftoff and processing. To address these issues, we developed a new series of robust and reusable inorganic templates based on high isoelectric point materials, including Al_2O_3 , MgO , and Y_2O_3 , which allowed for electrostatic self-assembly of silica-clad QDs on predefined arrays with high precision (~ 30 nm resolution). These inorganic templates offer several advantages over the original PDDA templates including better stability and higher refractive index and better integration with waveguides.

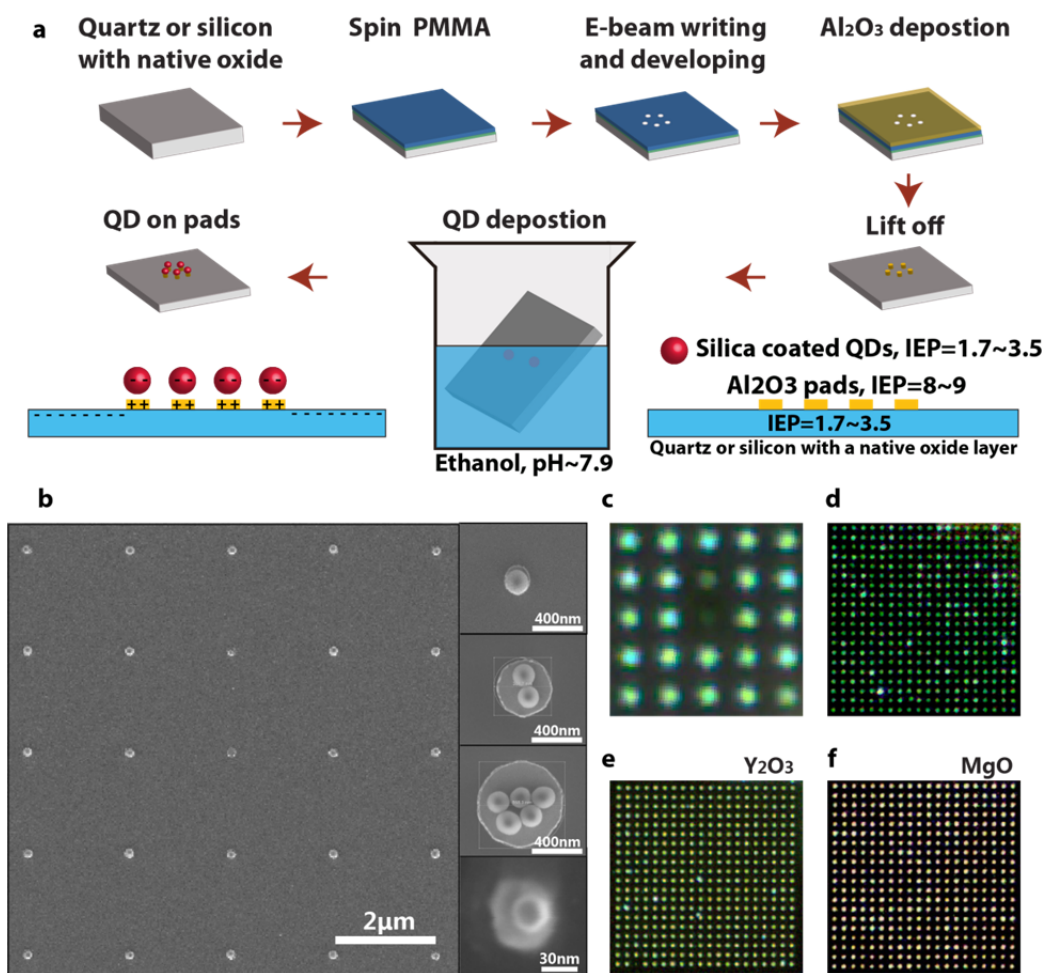


Figure 6: Electrostatic self-assembly for the arrays of single QDs.

(a) Scheme illustrating the fabrication and the self-assembly process; (b) scanning electron microscope (SEM) images of silica-clad QDs sitting on Al_2O_3 pads. Inset shows 160 nm silica-clad QDs on different size pads, and a 30 nm silica-clad QD on a 50 nm pad. (c) dark field images show the same deposition result as shown in the SEM image. (d,e,f) dark field microscope images of 160 nm silica-clad QDs on the 160 nm pads with a 2 μm pitch using different dielectric materials.

Under neutral conditions (pH~7), these high isoelectric point materials all exhibit positive surface charge, and thus can attract the negatively charged surface of the silica-clad QDs. The electrostatic bond strength is sufficient for normal sample handling and optical characterization, but the QDs can be easily removed by sonication while immersed in ethanol. Once cleaned, the template can be reused at any time and placed back into the QD solution for re-deposition.

To demonstrate this reusability, daily testing was performed over a one-month-long QD re-deposition experiment. A sample with Al_2O_3 pads was cleaned using acetone and ethanol and then dipped in the silica-clad QD solution overnight to allow for good coverage. The sample was then checked in a dark field microscope to determine the total QD pad coverage and the selectivity of pad bonding over substrate bonding (see figure 7). The same sample was then sonicated in ethanol to remove the QDs and new ones were deposited. This daily process of deposition and cleaning was carried out for one month. For the majority of depositions >95% pad coverage was achieved. The same sample was also retested five months later, and even after 150 days, the QD coverage remained high (>90%).

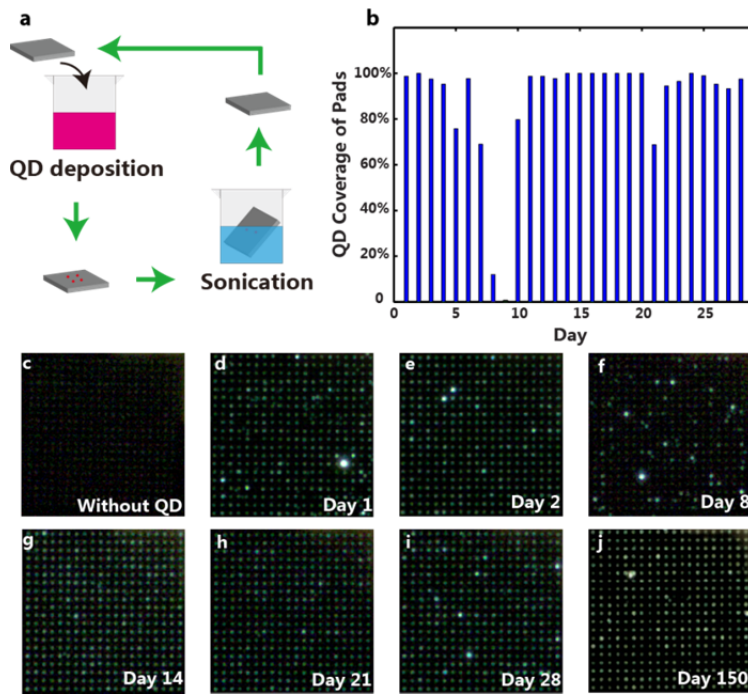


Figure 7: The reusability experiment for Al_2O_3 pad array sample.

(a) Experiment procedure. (b) QD deposition result for the one-month long test. (c) optical dark field image of the sample without QDs on. (d)-(j) the dark field images for the QD coverage. All of these eight images are taken on the same area from the same sample. Note that the reduced pad coverage on days 8 and 9 in (b) was due to contaminant build up which was easily removed by performing a more thorough cleaning (5 min acetone, 5 min methanol, 5 min ethanol) every three days.

Fully Automated, Large-Scale Array Characterization

To characterize the electrostatically self-assembled arrays of single silica-clad QDs, we built a custom characterization system combining a modular scanning confocal microscope and a Hanbury Brown-Twiss (HBT) measurement setup (see the Figure 8 a), which can also be adapted for lifetime and spectral measurements. This setup allows for the easy identification of pads with active QD emitters and performs

automated $g^{(2)}$ autocorrelation measurements from which we can infer the number of emitters in each shell, their lifetimes and quality (e.g. resistance to blinking and photobleaching). This setup also helps acquire meaningful statistics for other investigation, such as lifetime distributions to study Purcell enhancements.

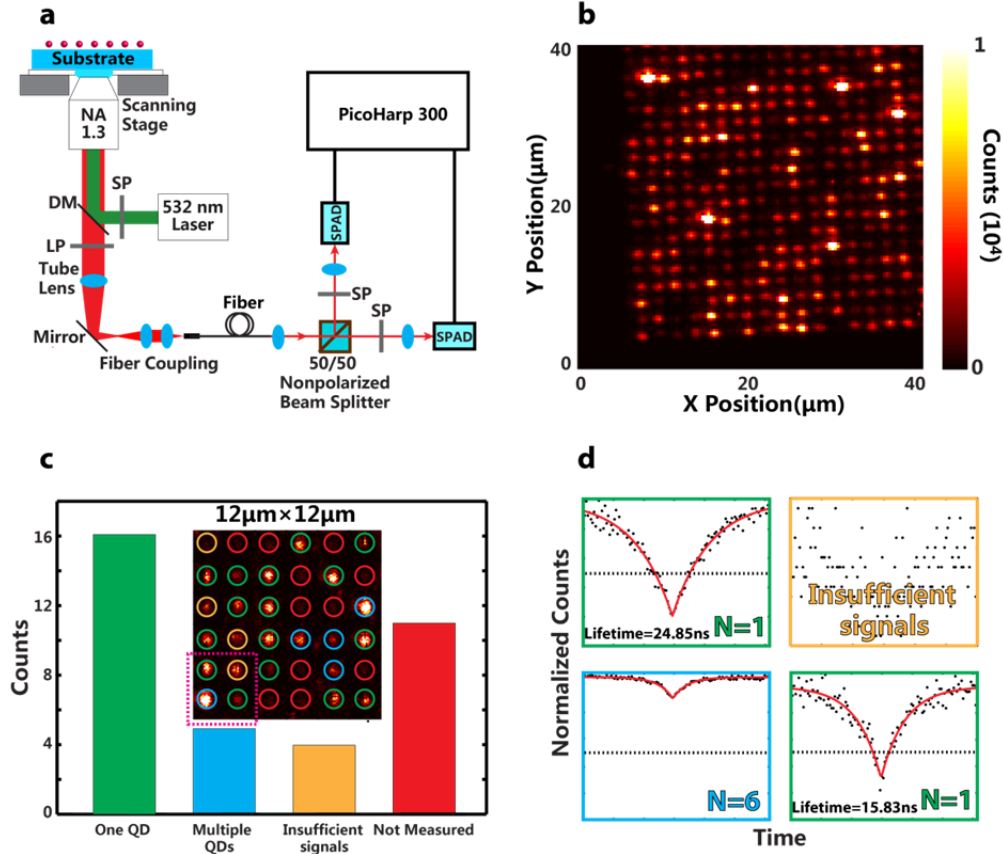


Figure 8: Anti-bunching experiment for the silica-clad QDs on predefined Al_2O_3 arrays.

(a) HBT Setup combined with scanning confocal microscope. (b) confocal scan image for a $40\mu\text{m} \times 40\mu\text{m}$ area of a $2\mu\text{m}$ pitch QDs arrays. (c) statistical results of the $g^{(2)}$ experiments for the inset confocal scan. (d) $g^{(2)}$ curves for the spots inside the dashed square in the scan image, dashed lines are $g^{(2)}=0.5$.

Scalable Process for QD Integration in Nanophotonic Structures

Using this self-assembly technique we demonstrated that silica-clad colloidal QDs can be easily integrated with nanofabrication processes. For example, by using a two-step lithography technique, gold nanorod antennas of various sizes were patterned on a silicon substrate

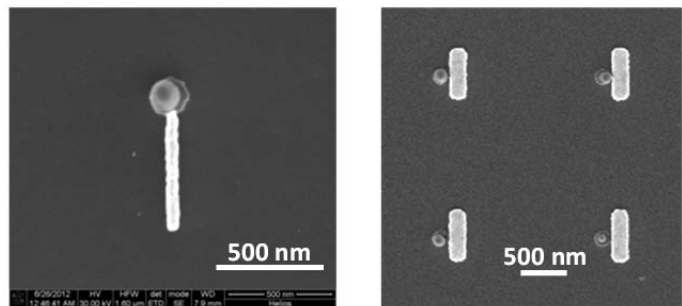


Figure 9: SEM images of QDs integrated with gold rods

followed by 200 nm diameter Al_2O_3 pads at varying distances from the nanorods antennas. An SEM of the resulting structure after electrostatic self-assembly of 160 nm diameter silica-clad QDs is shown in Figure 9, which clearly demonstrate that this technique allows for controllable positioning of single quantum emitters relative to nanophotonic structures. Also, due to the reusability of the template, repeated study of the same resonant nanostructure with different single emitters is possible; building such statistical data sets for single optical nanostructure could help bypass the need for ensemble measurements on many different structures (and the complications of their fabrication irregularities) to access the underlying optical resonances of each unique structure.

We also demonstrated a scalable process for embedding colloidal QDs in dielectric waveguides. Using the process shown in Figure 10 a, we successfully embedded single QDs inside dielectric waveguides over centimeter size chips. Single QD placement at waveguide intersections was easily accomplished by leveraging the high selectivity of electrostatic self-assembly. This process has the additional benefit of ensuring that all high temperature fabrication steps (such as curing PMMA e-beam resist) precedes QD integration, thus preventing damage to the colloidal QDs. Scanning confocal imaging was used to confirm the placement of QDs in the waveguide structure as shown in Figure 10 b.

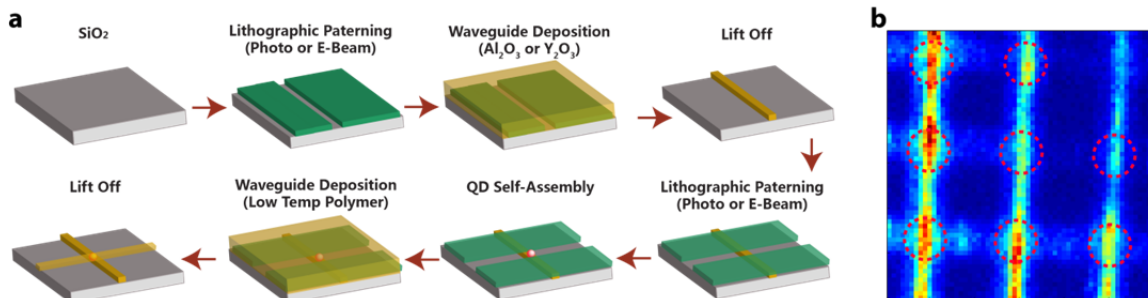


Figure 10: Embedding QDs at the intersection of dielectric waveguides.

(a) Process flow for fabrication of matrix-addressable waveguide architecture without compromising QD quantum efficiency. (b) Confocal scan image of the QDs embedded in the waveguide intersections.

Impact and Implications for Future Work

Having demonstrated a highly reliable and robust method for the study of silica encapsulated colloidal QDs, we are now focused on expanding this technique to other quantum emitters and material systems. Specifically, nitrogen vacancy centers in diamond nanocrystals have proven to be a robust, room temperature, single photon emitter. In contrast to colloidal quantum dots, NV centers exhibit significantly reduced

luminescence blinking, and do not suffer from oxidation related emission blue shifting or photo-induced bleaching. Given their intrinsically low IEP (~3, close to that of SiO₂) they are ideal candidates for our electrostatic self-assembly method as this will circumvent the need for silica encapsulation and will therefore greatly simplify the self-assembly process. In addition, we are currently investigating usage of our method on substrates with high IEPs such as Al₂O₃, Si₃N₄, and ITO. By using nanoparticle emitters with intrinsically high IEPs, such as MgO nanocubes and ZnO nanocrystals, we can expand the range of applicability of our self-assembly technique.

Personnel Supported

Faculty: Rashid Zia and Arto V. Nurmikko

Postdocs: Coung Dang

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Peer-Reviewed Publications

C. Dang, J. Lee, C. Breen, J. S. Steckel, S. Coe-Sullivan, and A. Nurmikko, **"Red, green and blue lasing enabled by single-exciton gain in colloidal quantum dot films."** *Nature Nanotechnology* **7**, 335-339 (2012).

Invited Papers

C. Dang and A.V. Nurmikko, **"Single-exciton gain enables red, green, and blue colloidal quantum dot lasers."** *SPIE Newsroom* DOI: 10.1117/2.1201208.004441 (2012)].

Presentations

2/27/12, **"Waveguide Integrated Colloidal Quantum Dot Emitters"**, M. Jiang, American Physical Society, APS March Meeting, Boston MA

Posters

9/03/12, **"Controllably Integrating Single Colloidal Quantum Dots into Dielectric Waveguides"**, M. Jiang, Near-field Optics, Nanophotonics and Related Techniques (NFO), Donostia - San Sebastian, Spain